

## **CHAPTER 4**

# **ANALYTICAL CHEMISTRY SUBGROUP**

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## **New Jersey Chromium Workgroup Report**

### **CHAPTER 4**

#### **Analytical Chemistry Subgroup**

##### **Charges Being Addressed**

###### 1. Certified Method

The Site Remediation and Waste Management Program has been accepting analytical results for hexavalent chromium using a non-NJDEP certified analytical method for Cr(VI) digestion. There is an USEPA-certified method available (Method 3060A). Should the Department mandate use of the USEPA method for hexavalent chromium determinations? What should the Department do about data obtained by the non-certified method the Site Remediation and Waste Management Program has been using for site decisions?

###### 2. Data Review and Acceptance

What should the Department policy be on analytical data where the associated quality assurance protocols are outside method limits?

###### 3. Additional Analytical Methods

USEPA Method 6800 “Elemental and Speciated Isotope Dilution Mass Spectrometry” is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. Should the OQA offer certification for USEPA Method 6800? If so, what should be the extent of its potential applications?

###### 4. Method Deficiencies

There is a question that the methods for the regulatory-approved methods of preparation and analysis of hexavalent chromium (USEPA Methods 3060A, 7196a and 7199) underestimate its in-situ concentration in certain types of soil. What are the circumstances where the low bias in hexavalent chromium measurements exist? Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI)) in sample preparation and/or measurement occurs?

###### 5. Quality Assurance Tools

The Department has proposed a collaboration with USEPA, National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health Sciences Institute (EOHSI) to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County, New Jersey that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?

## **6. Other Measurement Options**

Is it possible to develop a commercially available, NJDEP-certifiable method to replace the current method (Method 3060A)? If not, should speciation of hexavalent chromium continue to be performed should only total chromium be measured? Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing chromium remediation standards?

### **Summary**

- The Department has been using methods which have not been certified by the New Jersey Environmental Laboratory Certification Program to prepare non-aqueous samples for Cr(VI) measurements. The Department has been using both USEPA Method 3060A (USEPA 1995a) and NJDEP Modified Method 3060 (NJDEP, 1992). The Department's Site Remediation and Waste Management Program has recommended that only USEPA Method 3060A be used. The Subgroup concurs with the Site Remediation and Waste Management Program's recommendation to use only USEPA Method 3060A to prepare samples for the analysis of Cr(VI), and the Department should make plans to implement this policy for all new sampling endeavors. For those sites for which Department approved oversight documents exists, the Department shall notify the Responsible Parties and/or their representatives of the changes in analytical methodology prior to the next sampling activity at that site. Any corresponding oversight document shall be revised by the Responsible Party and/or its representatives to reflect the methodology change.
- Quality Assurance/Quality Control (QA/QC) data from past Cr(VI) analyses have shown that variations in sample matrices can result in biased results. The biased results can be attributed to both sample matrices and the specific analytical method used to test the sample. Because of these biases it is important that the QA/QC of methods be closely evaluated, most specifically the "Spike Recoveries." The Subgroup recommends that only Cr(VI) analytical results that have met the "Spike Recoveries" required in the analytical methods be used without qualification. As part of this recommendation, a Departmental Workgroup should be immediately established to define the data usability policy to be followed in the remediation decision processes. The Departmental Workgroup will consist of staff representing the Site Remediation and Waste Management Program (SRWMP), the Division of Science, Research and Technology, and the Office of Quality Assurance. The usability of data associated with spike recoveries outside criteria shall be determined on a case-by-case basis in concert with the recommended data usability procedure generated by the workgroup, except for samples where decisions are made for unconditional "No Further Action", in which case qualified data may not be used.
- The Subgroup recommends that samples be analyzed for Cr(VI) using a tiered approach that includes USEPA Method 7196A, USEPA Method 7199 and USEPA Method 6800 (Figures 4.1-4.5 at the end of this chapter). If the spike recovery obtained from USEPA Method 7196A is found acceptable, the analytical results from the associated samples are also acceptable. If the spike recovery is found outside limits, the NJDEP case team should

require a new sample digestate be reanalyzed using USEPA Method 7196A, as per the method requirements. If USEPA Method 7196A was again used and the spike recovery remains unacceptable, the NJDEP case team shall determine the usability of the data on a case-by-case basis using the data usability procedure described in this chapter. Further action may include using the data or requiring additional analysis using a different analytical method. If USEPA Method 7199 is used and the spike recovery obtained is found acceptable, the analytical results from the associated samples are also acceptable. If USEPA Method 7199 was used and the spike recovery is outside limits, remains unacceptable, the NJDEP case team should require a new sample digestate be reanalyzed using USEPA Method 7199, as per the method requirements. If the spike recovery remains outside limits, it is recommended that the NJDEP case team shall determine the usability of the data on a case-by-case basis using the data usability procedure described in this chapter. Further action may include using the data or requiring additional analysis using a different analytical method. Alternatively, a choice to begin the analytical process by using either USEPA Method 7199 or USEPA Method 6800 is an option. If the quality control requirements obtained from USEPA Method 6800 are found acceptable, the analytical results from the associated samples are also acceptable. If the quality control requirements are not fulfilled, new sample digestates must be reanalyzed using USEPA Method 6800, as per the method requirements. If the quality control requirements remain unmet, results may be qualified or rejected and usability shall be addressed by the NJDEP case team using the data usability procedure described in this chapter. Any decisions requiring additional analyses for Cr(VI) when corresponding matrix spike recoveries are outside method specified criteria will be made by the NJDEP case team, using the Department's data usability policy and on whether or not the data will be used in the issuance of an unconditional "No Further Action" or "Final Remediation Action" declaration.

- The Subgroup recommends that all samples analyzed for Cr(VI) also be analyzed for total chromium. The sample selected for the matrix spike shall also be analyzed for Eh and pH.
- The Department will arrange and participate in the development of speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices.
- The Department will fund a series of research projects to address key remaining questions and uncertainties. These projects will focus on areas where no existing information and/or data is available.

## **Responses to Charges**

### 1. Certified Method

*Should the Department mandate use of the USEPA Method 3060A for hexavalent chromium determinations?*

The Department should require the use of USEPA Method 3060A (USEPA, 1995a) for the digestion of non-aqueous matrices when samples are to be analyzed for Cr(VI). This policy should begin to be implemented immediately for all chromate ore processing residue (COPR) and non-aqueous matrices. For those sites for which Department approved oversight documents already exist (such as sampling plans and Quality Assurance Project Plans), the Department shall notify the Responsible Parties and/or their representatives of the changes in analytical methodology prior to the next sampling activity at that site. Any corresponding oversight document shall be revised by the responsible party and/or its representatives to reflect the methodology change. USEPA Method 3060A uses an alkaline digestion solution (0.28 M Na<sub>2</sub>CO<sub>3</sub>/0.5 M NaOH) at elevated temperatures for a proscribed period of time, and it is designed to dissolve both water soluble and water insoluble Cr(VI) compounds. USEPA Method 3060A provides the digestion step necessary when quantifying Cr(VI) in both COPR and non-COPRA sample matrices using USEPA Methods 7196A, 7199 and/or 6800.

USEPA Method 3060A is intended to minimize changes in the indigenous amounts of Cr(III) and Cr(VI) due to oxidation or reduction. In an oxidizing matrix Cr(III) converts to Cr(VI), and in a reducing matrix Cr(VI) converts to Cr(III). USEPA Method 3060A is effective for extracting Cr(VI) in COPR wastes (USEPA 1996b). However, applications of USEPA Method 3060A to soils and sediments containing matrix components that promote either oxidizing and/or reducing conditions may result in inaccurate data due to the interconversion of indigenous and spiked Cr(III) and Cr(VI) during the digestion (Vitale et al., 1994). The causes of such method performance issues are addressed in greater detail in the “Method Deficiencies” section below.

*What should the Department do about data obtained by the non-certified method the Site Remediation and Waste Management Program has been using for site decisions?*

The Department has used USEPA Method 3060, NJDEP Modified Method 3060 and USEPA Method 3060A when testing for Cr(VI). USEPA Method 3060 was withdrawn from the SW846 methods compendium for solid and hazardous waste in the late 1980s because of data documenting the failure of the method to accurately quantify Cr(VI) in samples containing a reducing condition. The Department needed to continue to analyze for Cr(VI), in the early 1990s the NJDEP developed a new method, designated NJDEP Modified Method 3060 to digest non-aqueous samples for subsequent Cr(VI) analysis.

In 1994 and 1995 the SW846 Inorganic Methods Workgroup met to review the NJDEP Modified Method 3060 in response to a proposal to include the method in the SW846 methods compendium. NJDEP Modified Method 3060 was brought to the SW846 Methods Workgroup by Rock Vitale, Environmental Standards, Inc. In 1996 the SW846 Inorganic Methods Workgroup approved the use of NJDEP Modified Method 3060 only after changes were made by

the Workgroup to the method's QA Section. These changes included the redigestion and reanalysis of the samples when Spike Recoveries are outside method limits.

In 1996 the Workgroup approved the newly revised method and designated it USEPA Method 3060A, for the Digestion of Non-Aqueous Samples for Cr(VI). The Department has continued to use NJDEP Modified Method 3060 rather than USEPA Method 3060A to respond to concerns surrounding long term data consistency. This policy was followed as the chemistry in NJDEP Modified Method 3060 differs subtly from USEPA Method 3060. NJDEP Modified Method 3060 lacks the addition of magnesium salt during the digestion which was a step that was designed to curtail the possible oxidation of Cr(III) to Cr(VI). NJDEP Modified Method 3060 also required shorter holding times which was designed to reduce the possibility of Cr(VI) reduction that could occur during the neutralization step/pH adjustment. It is unknown what affect the differences between Methods 3060 and 3060A may have on the measured amounts of Cr(VI).

It is the recommendation of the Subgroup that decisions made using data previously obtained shall remain. The data was obtained using the digestion methodology acceptable at the time (USEPA Method 3060 and NJDEP Modified Method 3060). Overall, the Subgroup considers that the decisions made in the past were based on the most reliable data available at the time. It is also the Subgroup's recommendation that if the Department elects to revisit previous decisions, new samples will be collected using the proposed list of analytical methods given in this report.

Additionally, analytical data obtained from the NJDEP Modified Method 3060 and USEPA Method 7196A that have yet to be validated shall be validated in accordance with the procedures discussed in the data validation documents developed by the Department (Appendices 6A and 6B). The data usability group will also consider modifications to the existing validation documents if warranted.

## 2. Data Review and Acceptance

*What should the Department policy be on analytical data where associated quality assurance protocols are outside method limits?*

The Analytical Chemistry Subgroup has developed a data decision tree to support a tiered approach for Cr(VI) analyses (see Figures 4.1-4.5 at the end of this chapter). A summary of the approach follows below.

Samples analyzed for Cr(VI) are first digested using USEPA Method 3060A. The digestate may be analyzed for Cr(VI) using either USEPA Method 7196A, 7199 or 6800. For an analytical result to found acceptable without qualification, the associated Quality Assurance (QA) results must meet the requirements of the selected analytical method. For Departmental purposes, QA results shall be focused on Spike Recovery data.

Method 3060A requires that the Cr(VI) matrix spike recovery meet the acceptance criteria within a range. The range of spike recovery must be no less than 75% and no greater than 125% of the

known spike. The method also requires redigestion and reanalysis when the matrix spike recovery fails to meet this criteria. This range of spike recovery is also applicable to two of the three analytical methods – USEPA Methods 7196A and 7199. USEPA Method 6800 has other quality control requirements that must be met for the resulting data to be accepted by the Department. Data usability, therefore, would follow the following sequence:

If USEPA Method 7196A is selected, the Spike Recovery data must be not be less than 75% or greater than 125%. If the Spike Recovery data fails to fall within this range, then a new digestate of the sample must be prepared and re-analyzed using USEPA Method 7196A, as per the method requirement. If the spike recovery data is again either less than 75% or greater than 125%, then the sample results will be qualified or rejected pursuant with the data validation Standard Operating Procedure (Appendix 6b). If it is determined that non-qualified/non-rejected data are required, then the NJDEP case team should require a new digestate of the sample be prepared and analyzed using either USEPA Method 7199 or 6800. If USEPA Method 7199 is selected, the spike recovery data for a sample must be not less than 75% or greater than 125 %. If the spike recovery data fails to fall within this range, the NJDEP case team should require a new digestate of the sample be prepared and re-analyzed using USEPA Method 7199, as per the method requirement. If the spike recovery data is again either less than 75% or greater than 125% then the sample results will be qualified or rejected. If it is determined that non-qualified/non-rejected data are required, then the NJDEP case team should require a new digestate of the sample be prepared and analyzed using either USEPA Method 6800. When USEPA Method 6800 is selected, the quality control requirements associated with this method must be met. If the quality control requirements are still not met, then the sample results will be qualified or rejected. Data usability will be determined using the data usability policy to be developed by the Department.

Flow charts indicating the sequence of how the analytical methods to be used under the conditions of the acceptable and unacceptable matrix spike recoveries appear in Figures 4.1-4.5 at the end of this chapter. There may be instances where, even after redigestion and re-analysis, the percent recovery of a matrix spike fails to meet acceptance criteria. While data may be qualified or rejected, it is possible that data may be used or additional Cr(VI) analyses may not be required. The Department policy on how these data are to be handled shall be defined in the data usability policy to be developed by the Department.

A major component in the field of data validation (of environmental sample data) is how noncompliant QA results are handled. The USEPA has functional guidelines published to address how data are to be reviewed. In the guidelines, data outside method published criteria may be qualified, rejected, or in some instances, deemed acceptable. Acceptance criteria for QA parameters are frequently expanded from the method specified criteria and it is the expanded criteria that are used to make data validation decisions. For instance, in the USEPA Statement of Work (USEPA, 2002), the method-specified criteria for the matrix spike recovery is greater than or equal to 75% and less than or equal to 125%. In the USEPA contract laboratory program guidelines (USEPA, 2002), it is stated that if the matrix spike recovery is 30-75% and the sample results are above the minimum detection limit, then the results are qualified. Additionally, if the matrix spike recovery is 125%, non-detect results are not qualified but useable.



The SRWMP has data validation protocols in place to handle situations where QA results do not meet criteria for numerous compounds represented by the routine analyses performed for the program (Appendices 6A and 6B). Both the USEPA and the Department's Office of Quality Assurance have approved the data validation protocols for use. The validation process is based on spike recovery data and the concentration of the matrix spike relative to the concentration of the sample. As a result of the validation, it may be determined that the data are qualified or rejected due to unacceptable matrix spike recoveries. However, data qualified or rejected due to matrix spike criteria outside method specified levels does not necessarily render the same associated sample result unusable even though the actual amounts of Cr(VI) in the samples could have increased uncertainty. Other factors such as site-specific concerns and additional analytical results are frequently considered before reanalysis of a sample is required. Professional judgement is required when interpreting the findings brought forth from the data validation and deciding how best to proceed with a remediation. Examples where professional judgement is used are as follows:

Example 1: Samples are analyzed by USEPA Method 7196A. The Cr(VI) matrix spike recovery is 60%. The Cr(VI) results from samples associated with the matrix spike are all above the applicable remediation standard. Samples were redigested and re-analyzed as per method requirements with the same end results. The area of concern represented by the samples would require remediation. There would be no need to reanalyze samples by another method.

Example 2: Samples are analyzed by USEPA Method 7196A. The Cr(VI) matrix spike recovery is 30%. The Cr(VI) results from samples associated with the matrix spike are slightly below the applicable remediation standard. Samples were redigested and re-analyzed as per method requirements with the same end results. Total chromium was the only other analysis performed on the samples. Total chromium results were slightly below the remediation standard. The samples would be redigested and re-analyzed by USEPA Methods 7199 and/or 6800.

In summary, decisions concerning the use of qualified or rejected data shall be handled consistently using the protocol specified in the proposed data usability policy. Redigestion and re-analysis may or may not be required. In some instances, qualified sample data obtained from USEPA Method 7196A may be all that is needed to make a remedial decision, except in instances where unconditional "No Further Action" decisions are being requested. In other instances, it may be imperative to know what the effects of the matrix are on the sample results and USEPA Method 6800 may be selected.

It is the opinion of the Subgroup that USEPA Method 6800 can generate reliable data where the sample matrix is either highly reducing or oxidizing. USEPA Method 6800 uses speciated isotope dilution mass spectrometric techniques and the method has shown that it is capable of identifying and correcting for chromium species conversion (Kingston et al, 1998). However, not all the literature reviewed during the Subgroup's activities support this opinion. For instance, a recent paper questioned the efficacy and scope of application of this methodology to completely correct for conversion of Cr(VI) to Cr(III) in highly reducing soil conditions (Tirez et al, 2003). But overall, the literature reviewed during the Subgroup's activities supported the use of USEPA Method 6800 to address the conversion of Cr(VI) between the collection and analysis of a sample.

The Subgroup recommends that the Department should establish a more formal policy describing data usability. It is acknowledged that no such policy currently exists for any contaminant. Such a policy will provide the procedures and standards needed to determine when data can be used that has not met the “Spike Recoveries” required in the analytical methodology. However, this policy is intended only for data that is not used to make Unconditional No Further Action decisions. The Department has included a process for addressing its emerging Quality Assurance (QA) issues in the FY05/06 Departmental Quality Management Plan (QMP). The process includes submittal of suggested issues to the Department Quality Assurance Officer (DQAO), review of the submitted issues by the DQAO, submittal of issues needing attention to the Department’s Senior Staff for approval to establish a temporary workgroup, and selection of the workgroup members by the Senior Staff and the DQAO. The Subgroup recommends that the Department use this process immediately to address the updating of its current data usability policies relating to COPR Cr(VI) analytical results.

Because of the complexities surrounding the Cr(VI) analyses and subsequent data usability issues, it is imperative that laboratories performing Cr(VI) analyses should maintain an open line of communication with the Department and/or responsible parties. In those instances where samples are to be re-digested and re-analyzed, the Department may be contacted to determine if accurate Cr(VI) measurements from the samples in question are needed. As part of the remedial process, the Department (i.e. technical coordinators, case managers) shall evaluate the available data incorporating the criteria set forth in the data usability protocol to determine if further testing is necessary. There may be situations where, based on the analytical results of other samples and/or other parameters, remedial decisions can be made without having Cr(VI) results that have passed the spike recoveries for a given recommended analytical method. As a result, the Department may decide that there is no need for a laboratory to proceed with further analytical testing. The exception is in cases where unconditional decisions are being requested, in which cases no qualified or rejected data shall be used to make these determinations.

The Subgroup also recommends that careful attention be given to the definition of a Sample Delivery Group (SDG). That is, what constitutes those samples that are grouped together for subsequent analysis. USEPA Methods 3060A, 7196A and 7199 all call for one sample from the SDG to be spiked with a known amount of Cr(VI); the results for that sample are used to evaluate the efficacy of data for the entire SDG. Since studies have shown that spike recoveries vary with the nature of the sample matrix, only samples with similar matrices shall be included in any one SDG.

### 3. Additional Analytical Methods

*Should the Office of Quality Assurance offer certification for USEPA Method 6800?*

USEPA Method 6800 “Elemental and Speciated Isotope Dilution Mass Spectrometry” (USEPA, 1997) is approved and included in SW846 for the analysis of speciated metals, including chromium. The Office of Quality Assurance (OQA) does not currently offer certification for USEPA Method 6800. The OQA uses N.J.A.C. 7:18, Regulations Governing the Certification of Laboratories and Environmental Measurements, to administer the State of New Jersey’s

Environmental Laboratory Certification Program. N.J.A.C. 7:18 adopts-by-reference the SW846 analytical methods. Therefore, the Department has the existing authority to add USEPA Method 6800 to the list of methods offered for New Jersey Environmental Laboratory Certification. The OQA will add USEPA Method 6800 to its responsibilities effective immediately. Additionally, several academic and commercial laboratories have indicated their willingness to become certified for USEPA Method 6800.

*If so, what should be the extent of its potential applications?*

USEPA Method 6800 could be used when either USEPA Method 7196A or 7199 is used to test for Cr(VI) and the spike recovery results fall outside the method's acceptable limits. However, USEPA Method 6800 is acceptable for analyzing Cr(VI) in all instances when the regulated community chooses to forgo the use of either USEPA Method 7196A or 7199.

#### 4. Method Deficiencies

Empirical data have indicated transformation of chromium species may be occurring or may have occurred in certain soil types both environmentally and during sample analysis. Cr(VI) under certain conditions can be reduced to Cr(III), resulting in less Cr(VI) than may actually be present (low bias) while Cr(III) can be oxidized to Cr(VI) resulting in more Cr(VI) than may actually be present (high bias) (James et al., 1997).

*What are the circumstances where the low bias in hexavalent chromium measurements exists?*

Over the past years, data from the analysis of COPR material has, in many cases, yielded satisfactory matrix spike recoveries. Analytical results comparing USEPA Method 7196A (the traditional colorimetric method) to USEPA Method 6800 (the speciated isotope dilution mass spectrometry method designed to correct for species transformation) indicate COPR sample concentrations of Cr(VI) can be virtually identical for many samples (Huo et al., 2000). But in those cases where the Cr(VI) matrix spikes yield percent recoveries less than the method acceptance criteria, there is a cause to be concerned, as the measured values may indicate less Cr(VI) than is present in the sample collected.

There are several possible causes for reduction of Cr(VI) to Cr(III). The chemical nature of the matrix itself could be providing the necessary conditions under which reduction of Cr(VI) in the matrix spike occurs. Researchers have stressed the necessity to characterize the soil matrix by determining Eh (oxidation-reduction potential), pH, total organic carbon, ferrous iron, and sulfide to evaluate its potential to interconvert Cr(III) and Cr(VI) (Vitale et al., 1997). If a reducing condition exists as defined by the chrome Eh-pH phase diagram (Figure 4.6 at the end of this chapter); the presence of TOC, S<sup>2-</sup>, Fe(II) and/or acidic conditions then the potential for the sample to reduce the laboratory Cr(VI) spike or not sustain the existence of Cr(VI) in the sample's natural environment also exists (James 1997). The presence of iron in different species and organic matter has also been shown to interfere with Cr(VI) by reducing it during measurement by USEPA Method 7196A (Huo et al., 1998). Data indicates that Fe(II) and sulfides can decrease the recoveries of Cr(VI) spikes. Fe(III) has been shown to oxidize DPC (diphenylcarbazide), thus not allowing it to react with all of the Cr(VI) in the sample. The result

of this oxidation reduces the efficiency of the matrix spike recovery. Additionally, during this oxidation process, Fe(III) is reduced to Fe(II) which in turn could reduce Cr(VI).

Reduction of Cr(VI) occurs when reducing material from the matrix is allowed to react with Cr(VI) during the neutralization process. Method-induced reduction of Cr(VI) to Cr(III), either by digestion or measurement, has been documented (Huo and Kingston, 2000). It has been recommended by analysts experienced in the analysis of Cr(VI) in soils that for future Cr(VI) analyses the digestion solution should be neutralized immediately before measurement as Cr(VI) has been observed to reduce during neutralization.

The comparisons and discussions of the analytical techniques have focused thus far mostly on USEPA Methods 7196A and 6800. Much of the reduction is believed to occur due to the presence of reducing material during the digestion and/or neutralization process. USEPA Method 7199 (USEPA, 1996a) removes some potentially reductive species through use of a guard column in the front end of the instrumentation. Studies conducted by the NJDEP Laboratories (NJDEP, 1993) reported that for comparable sample analyses of Cr(VI), digests yielded higher results by Method 7199 than by Method 7196A (USEPA, 1995b), although the lowest percent recovery noted was 74% using USEPA Method 7196A while all other recoveries for both USEPA 7196A and 7199 were within the 75% to 125% acceptance criteria. USEPA Method 6800 may be able to be used to gain better information relating to species interconversion. This Subgroup recommends that laboratories experiencing unacceptable matrix spike recoveries with samples analyzed and reanalyzed by USEPA Method 7196A are to re-digest the samples by USEPA Method 3060A and re-analyze the samples by USEPA Method 7199. Laboratories should also have the option to perform Cr(VI) analyses by USEPA Method 7199 or USEPA Method 6800 from the outset. Additionally, to help determine if the matrix is reducing in nature, laboratories shall be required to perform basic testing (eH, pH, and possibly TOC, sulfides and total iron) on select samples and on all matrix spike samples.

*Are there any conditions under which high bias (resulting from oxidation of Cr(III) to Cr(VI) in sample preparation and/or measurement occurs?*

Cr(III) can be oxidized to Cr(VI). However, the extent of oxidation of Cr(III) depends on the chemical form of the Cr complex in which it exists. Cr(III) and freshly precipitated Cr(OH)<sub>3</sub> are relatively easy to oxidize, while (Cr<sub>2</sub>O<sub>7</sub>)<sup>-2</sup> and aged Cr(OH)<sub>3</sub> are resistant to oxidation. Oxidation is more likely to occur during the digestion step where conditions are thermodynamically favorable.

There are instances where, under the correct environmental conditions, that oxidation of Cr(III) may occur simultaneously with the reduction of Cr(VI) (Vitale et al., 1994). It is the Subgroup's opinion that this can be documented by using USEPA Method 6800 to track species interconversion.

## **5. Quality Assurance Tools**

*The Department has proposed a collaboration with EPA, NIST and EOHSI to develop a reference material of defined Cr(VI) concentration using a source material from Hudson County,*

*New Jersey that can be used to assess the efficacy of future Cr(VI) measurements. Should such a reference material be developed?*

The Subgroup recommends that a project be completed to develop reference materials. The Department has an existing proposal (See Research Section), managed by OQA, which has been agreed to by the USEPA, the National Institute of Standards and Technology (NIST) and the Environmental and Occupational Health and Science Institute (EOHSI). It is recommended that the Department supply some of the funding needed to complete the project; NIST has funding to prepare the first chromium sample for homogenization and distribution for round-robin analyses. Activities to initiate this project should begin by June 2005.

## **6. Measurement Options**

*While advanced analytical methods (such as USEPA Method 6800) exist to better analyze the concentration of this species, is it possible to develop a commercially available, NJDEP-certifiable method to replace the current digestion method (USEPA Method 3060A)?*

The Subgroup is not aware of any procedure to quantitatively remove Cr(VI) from soil matrices while maintaining indigenous Cr(III) and Cr(VI) concentrations other than USEPA Method 3060A. However, it may be possible that another method that can quantitatively remove Cr(VI) from non-aqueous samples without being subject to specie interconversion can be developed. Research on options for sample preparation as well as in-situ methods of analysis are part of a separate list of research proposals.

*If not, the question is: should speciation of hexavalent chromium continue to be performed, or is it more protective to measure total chromium only?*

Cr(VI) analyses should still be performed using the current digestion and analytical methods available. For COPR matrices, using the combination of USEPA Methods 3060A and 7199 has shown to yield accurate and reproducible results (Kingston et al., 1998). This subgroup also recommends that in addition to Cr(VI) analyses, total chromium analyses be performed simultaneously on all samples. Both methods should yield sufficient data upon which remedial decisions could be made.

*Are there any known biases to the measurement of total chromium in soil that would prevent its use in establishing Cr remediation standards?*

An option to the direct measurement of Cr(VI) is to measure total Cr by USEPA Methods 3050/6010B or USEPA SOW ILMO5.2. For most matrices, review of Performance Testing data show that Total Cr measurements have less uncertainty and better accuracy than measurements of Cr(VI). However, the Department (Site Remediation and Waste Management Programs) has observed Total Cr empirical data with both high and low biases. The Subgroup recommends that Cr(VI) measurements be continued, and that Total Cr measurements also be required on all samples requiring Cr(VI) analyses.

The Subgroup also recommends that a research project be completed to address the analytical uncertainties. Comparisons of USEPA Methods 7196A, 7199, and 6800 shall be performed to determine differences, if any, in analytical precision and accuracy. Total chromium and material left on filters would be analyzed in parallel to provide information on mass balance and species conversion.

## **Research**

The Subgroup recommends that the following questions be considered through the use of research projects.

*After the digestion of soil samples containing Cr(III) and Cr(VI) using USEPA Method 3060A, which of the following three analytical methods best responds to the interconversion of Cr(III) and Cr(VI) in reducing and oxidizing soils?*

- Method 6800, Elemental and Speciated Isotope Dilution Mass Spectroscopy
- Method 7199, Determination of Hexavalent Chromium in Drinking Water Ground Water and Industrial Effluents by Ion Chromatography
- Method 7196A, Chromium (Colorimetric)

*How is the oxidation/reduction potential of chromium contaminated soil determined and are field measurements and laboratory measurements similar?*

The pH and eH of soil samples should be measured in the field and at the laboratory. The measurements must be made with calibrated instruments and the times recorded. The procedure is described in USEPA Method 3060A. These measurements should be taken for the samples used in first project listed above.

*Is there another digestion method that will remove Cr from soil without changing the indigenous content of Cr(III) and Cr(VI)?*

A detailed search of literature should be conducted to identify other possible methods. If methods are found, research should be conducted to determine if these methods are improvement over USEPA Method 3060A.

*Is there an analytical method that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion?*

- Evaluation of analytical methods that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion is needed. It is necessary to investigate the availability of methods that do not involve wet chemistry to address the concerns with interconversion and matrix spike recoveries. Researchers have investigated the use of a wide range of X-Ray methods for in-situ metals measurements. This research project should include use of the COPR matrix. These techniques would be able to determine worst case scenarios without first digesting the COPR waste into the

aqueous phase where reduction and/or oxidation could potentially inter-convert between the species present.

Research utilizing these methods would evaluate the ability of a solid-state analytical method to make in-situ measurement of Cr(VI) in soils and sediments.

The next step of the research project would characterize the Cr(III) and Cr(VI) ratio in COPR waste at the major waste sites in Hudson county. This information could then be used in the analysis of soils and sediments to determine Cr (VI) in soils and sediments. Additional methods that are capable of determining Cr(III) and Cr(VI) in soils without digestion should be explored and pursued.

*How can Cr(VI) measurements in non-aqueous media be improved?*

Evaluation of the efficacy of measurements of Cr(VI) in non-aqueous media such as soils and sediments would be aided by the availability of a reference material containing a known amount of Cr(VI). The development of reference material with defined species-specific Cr concentrations faces a number of technical challenges, including long-term specie stability and the potential for both the nature of the sample matrix and/or the analytical methods used for detection and quantitation to influence final measured results.

Agreement has been reached between a project team comprised of staff from the New Jersey Department of Environmental Protection, United States Department of Commerce - National Institute for Standards and Technology (NIST), United States Environmental Protection Agency, and the Environmental Occupational Health Sciences Institute – Rutgers University to develop a series of reference materials derived from different types of soils and/or sediments. The first sample in this series will be collected at a site in New Jersey, homogenized at a United States Geologic Survey facility, and aliquots distributed for an interlaboratory evaluation study to selected participating government, academic and commercial laboratories. The methods used for sample preparation and analysis of this material by each laboratory will be carefully monitored. Results will be evaluated by the project team, and the product, containing a description of the type of soil from which it was derived and containing a Cr(VI) concentration with defined limits of uncertainty, will be made available for sale by NIST.

## **Recommendations**

Programmatic:

- OQA will add USEPA Method 6800 to its list of certifiable analytical methods.
- USEPA Method 3060A will be used for digestion of all future soil samples for Cr(VI) analysis.
- A tiered approach to selection of determinative methods for Cr(VI) will be used as per Figures 4.1-4.5 (at the end of this chapter).

- USEPA Method 6800 could be used when sample digests have been analyzed by either USEPA Method 7196A and/or USEPA Method 7199 and the spike recoveries are less than 75% or more than 125%. USEPA Method 6800 may also be used initially.
- The Department will develop a data usability policy to permit the use of Cr(VI) analytical data that has not met the "Spike Recoveries" given the analytical methods. The Policy will permit the use of this data when it is not used for unconditional "No Further Action" decisions. The decision to either use or not use the data will be made by the Department in consultation with Responsible Parties.
- Total chromium will be analyzed concurrently with Cr(VI) for all samples.
- Measurements of the oxidative/reductive (Eh and pH) properties of the soil matrix will be made for all samples from sites with oxidizing or reducing conditions. Measurements will be made in the field and/or on receipt at the laboratory.
- Spike recoveries must meet the requirements stated in the analytical measurements for the Cr(VI) results to be acceptable without qualification.
- The Department will arrange and participate in the development of speciated reference materials to be used when analyzing for Cr(VI) in non-aqueous sample matrices. Once available, this reference material will be analyzed with every SDG.
- Careful attention should be given to the definition of a SDG; that is, what constitutes those samples that are grouped together for subsequent analysis. The SDG will consist only of samples of a similar matrix type.
- Decisions made using data previously generated by other analytical methods shall remain. If the Department elects to revisit previous decisions, new samples shall be collected using the proposed list of analytical methods given in this report.

Research:

- Comparison of analytical methods used to detect Cr(VI) in soil samples  
A research project should be designed to answer the following question:  
After the digestion of soil samples containing Cr(III) and Cr(VI) using USEPA Method 3060A, which of the following three analytical methods best responds to the interconversion of Cr(III) and Cr(VI) in reducing and oxidizing soils?  
Method 6800, Elemental and Speciated Isotope Dilution Mass Spectroscopy  
Method 7199, Determination of Hexavalent Chromium in Drinking Water  
Method 7196A, Chromium (Colorimetric)
- Evaluation of analytical methods that can determine Cr(III) and Cr(VI) in reducing and oxidizing soils without digestion is needed. It is necessary to investigate the availability of methods that do not involve wet chemistry to address the concerns with



interconversion and matrix spike recoveries. Researchers have investigated the use of a wide range of X-Ray methods for in-situ metals measurements. This research project should include use of the COPR matrix. These techniques would be able to determine worst case scenarios without first digesting the COPR waste into the aqueous phase where reduction and/or oxidation could potentially inter-convert between the species present.

Research utilizing these methods would evaluate the ability of a solid-state analytical method to make in-situ measurement of Cr(VI) in soils and sediments.

The next step of the research project would characterize the Cr(III) and Cr(VI) ratio in COPRA waste at the major waste sites in Hudson county. This information could then be used in the analysis of soils and sediments to determine Cr (VI) in soils and sediments. Additional methods that are capable of determining Cr(III) and Cr(VI) in soils without digestion should be explored and pursued.

- Examination of other digestion methods that will remove chromium from soil without changing the indigenous content of Cr(III) and Cr(VI). A detailed search of literature should be conducted to identify other possible methods. If methods are found, research should be conducted to determine if these methods are improvement over USEPA Method 3060A.

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Figure 4.1. Procedure for analytical method selection to analyze Cr(VI)

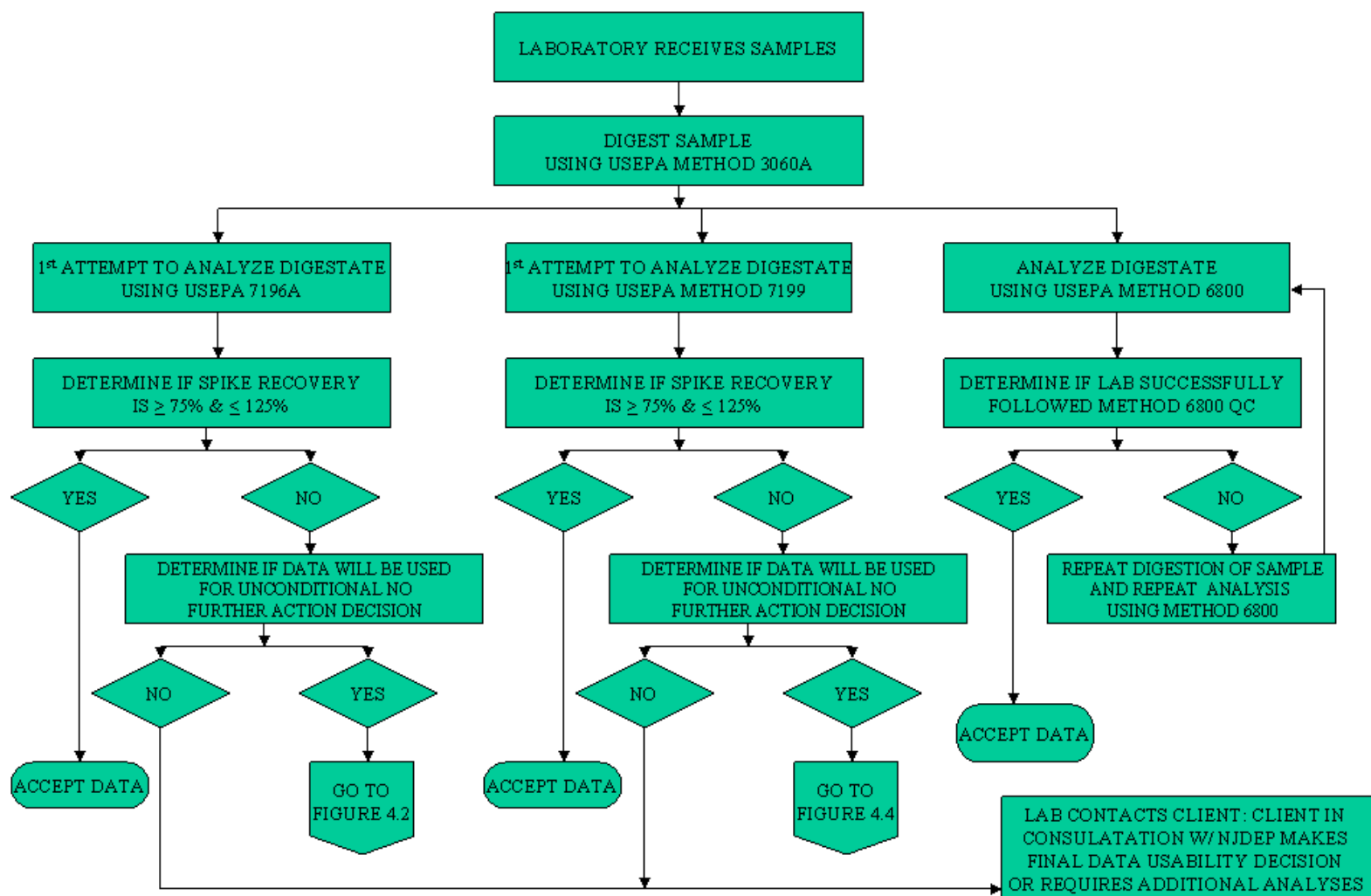


Figure 4.2. Procedure for analytical method selection to analyze Cr(VI) when 7196A fails quality control

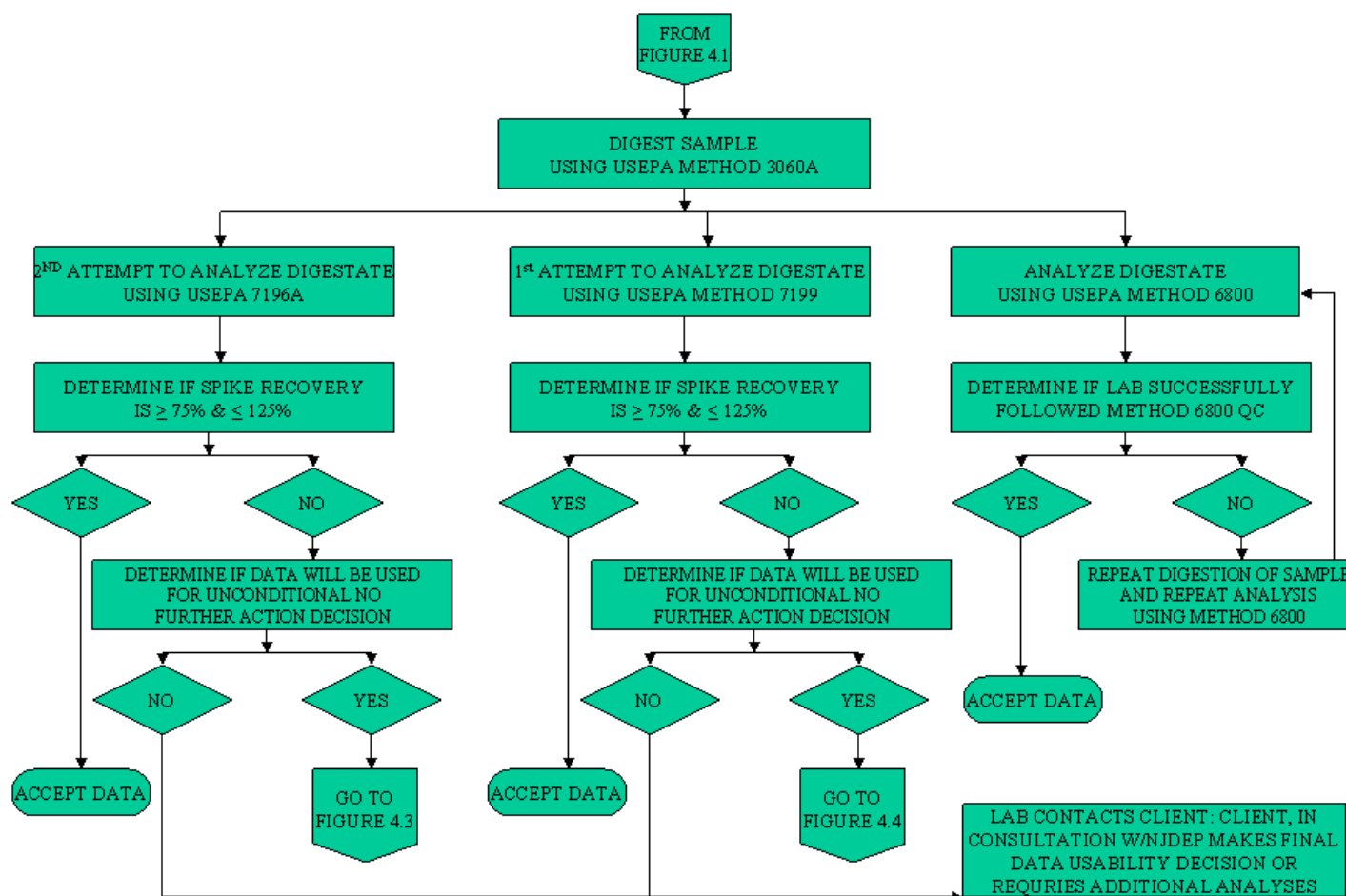


Figure 4.3. Procedure for analytical method selection to analyze Cr(VI) when 7196A fails quality control a second time.

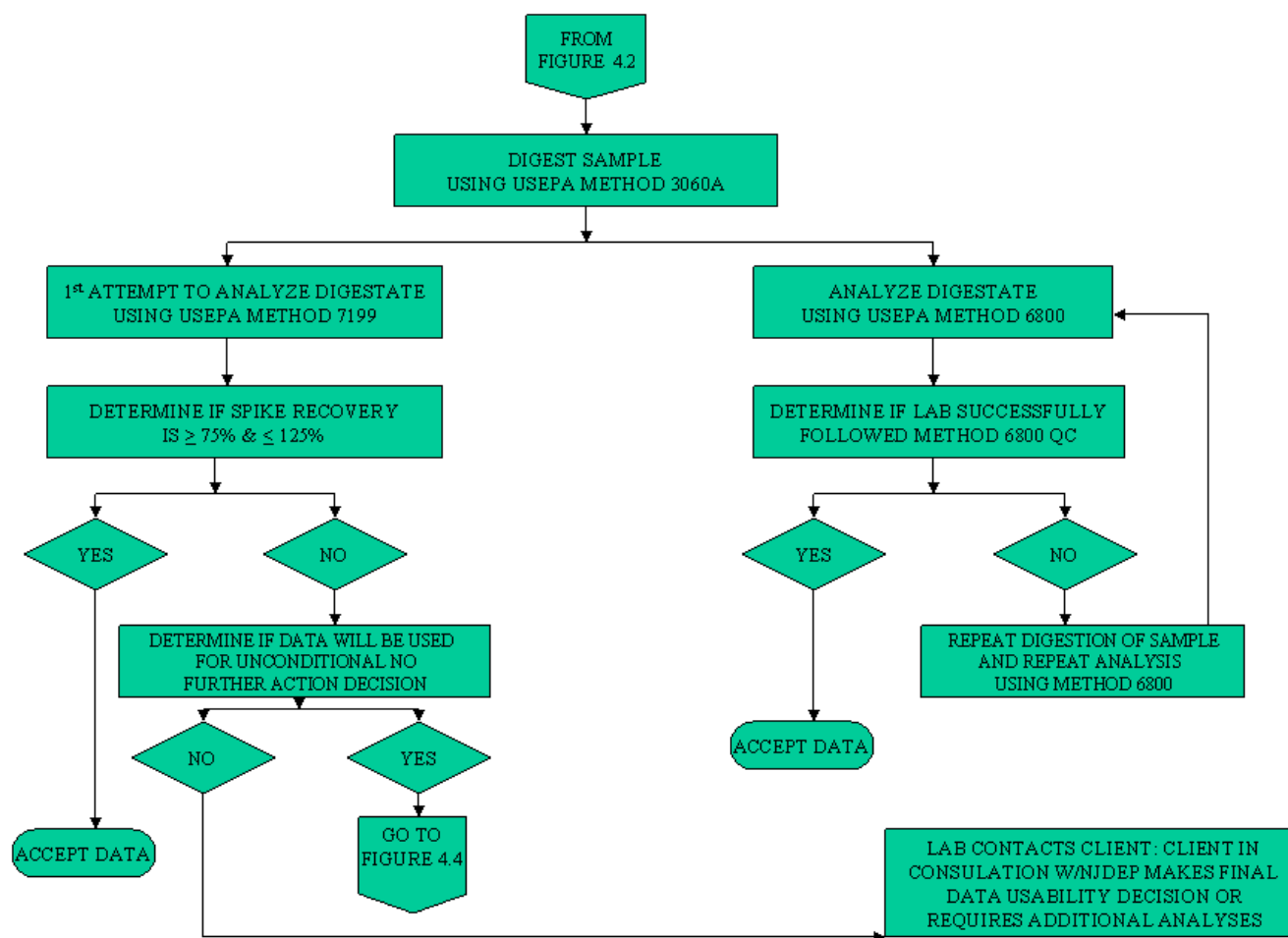


Figure 4.4. Procedure for analytical method selection to analyze Cr(VI) when 7196A and/or 7199 fail quality control once or twice.

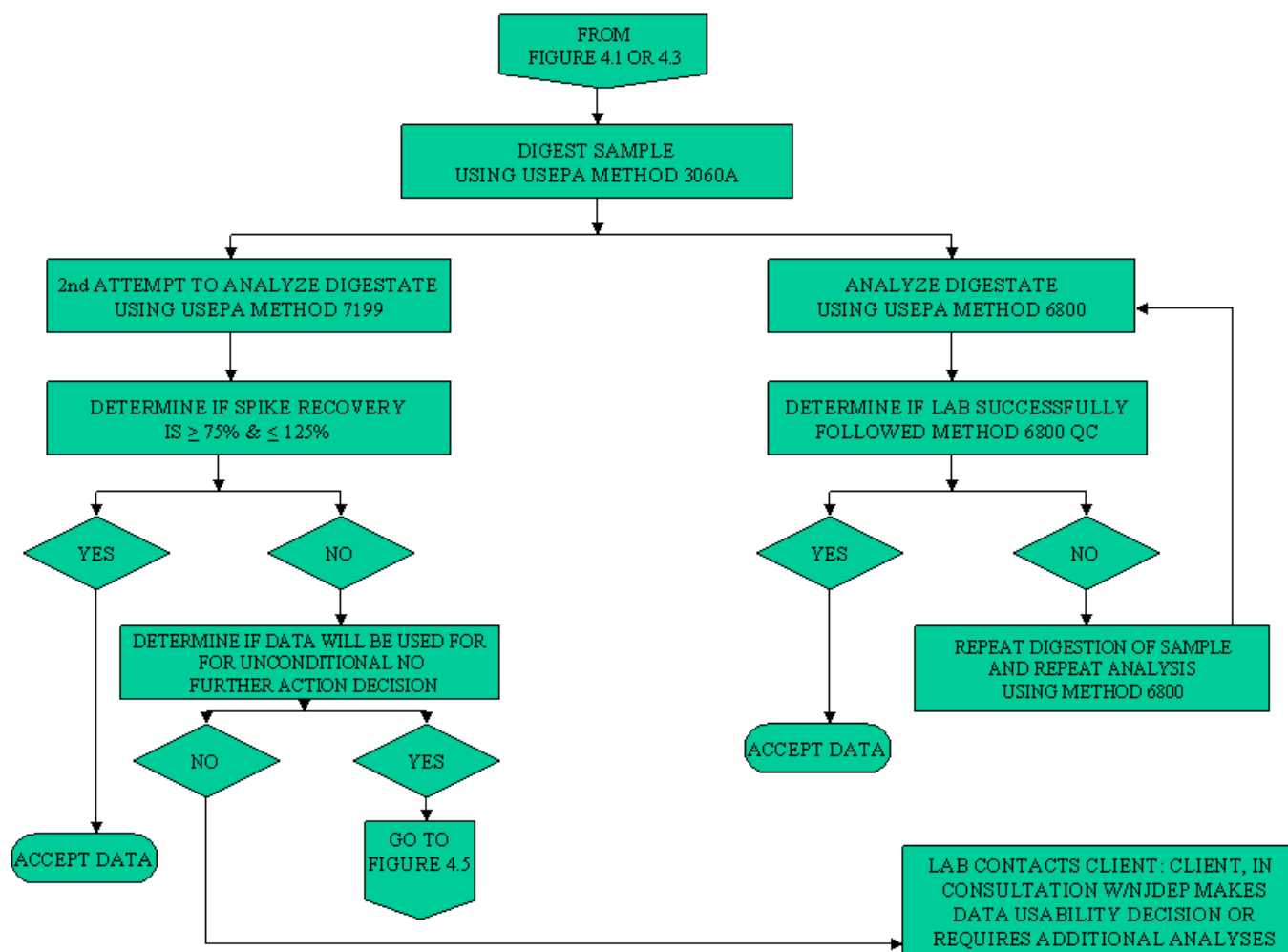


Figure 4.5. Procedure for analytical method selection to analyze Cr(VI) when 7196, 7199 and/or 6800 fail quality control.

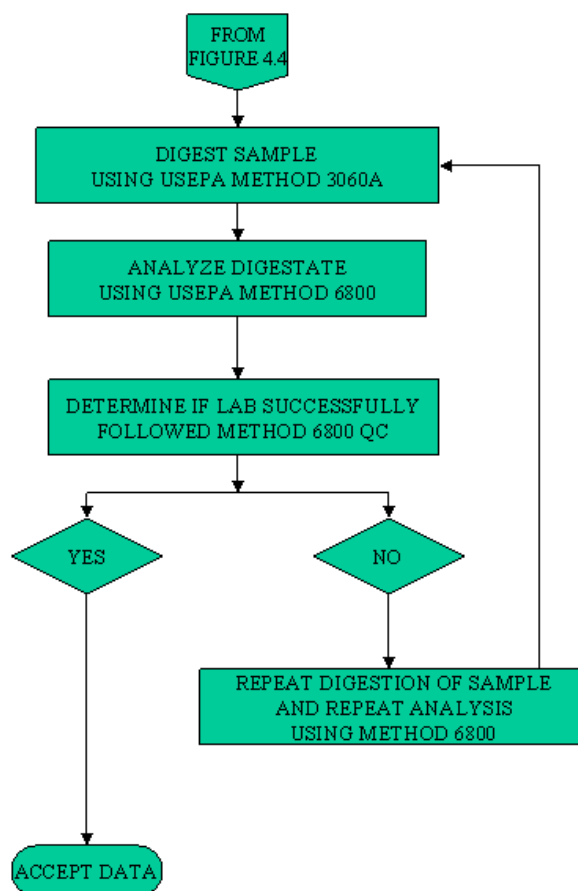




Figure 4.6 Eh/pH Phase Diagram

